

Bose-Einstein Condensation Picture of Superconductivity in High and in Low-Temperature Superconductors (Dilute Metals).

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Structures and parameters of some high and low temperature superconductors (HTSC, LTSC) are considered basing on the alternative estimate of the O^{2-} ion radius magnitude ($0.5 - 0.6$ Å). Phase transitions into the superconducting state are considered as the Bose-Einstein condensation (BEC). The super HTSC with $T_c = 371$ K ($YBa_2Cu_3Se_7$) and $T_c \sim 400$ K ($Ag_2(Ag_3Pb_2H_2O_6)$), and LTSC with $T_c \sim 0.3$ K ($SrNb_xTi_{(1-x)}O_3$) are shown to be of the BEC type. Instability of the structure of the first one results from higher magnitude of the Se^{2-} ion radius in comparison with the O^{2-} radius. The second one forms quasi one-dimensional structures and is rather impractical. The electron density and the effective mass are estimated for some stoichiometric and non-stoichiometric (nano-composite) high temperature superconductors, which have some peculiar features. Large effective masses can indicate existence of polarons (bipolarons) in such systems. Some new superconductors (Mg_xWO_3).

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The problem of HTSC physical mechanism remains open up to now. Fabrication of superconductors with $T_c > 300$ K or at least confirmation of information on unexpected synthesis of such materials somewhere would be extremely important as for physics so for electronics and electro-and magneto-energetics. It is quite possible that the first communication on discovery of a material with $T_c = 371$ K [1] was not confirmed because of instability of materials and irreproducibility of synthesis. Oxygen in $YBa_2Cu_3O_7$ was substituted with selenium in $YBa_2Cu_3Se_7$ in this case.

1). One of the main reasons of the current situation is a use of the traditional magnitude of 1.4 Å for the oxygen ion O^{2-} radius instead of the realistic in our opinion value of $0.5 - 0.6$ Å [2]. It is very important also the closeness of the radii $r_{O^{2-}}$ and r_O and relation $r_{Me} \gg r_{Me^{2+}}$. A cardinal transformation of the oxide electronic structure due to this conjecture is depicted schematically in Fig. 1 a), b). An instability of the structure occurs due to a substitution of O^{2-} by Se^{2-} ions with radius, which is twice as large as for the former. Structures of the stoichiometric $YBa_2Cu_3Se_7$ and nonstoichiometric ($Ag_2(Ag_3Pb_2H_2O_6)$) with $T_c > 400$ K [3] are presented in Fig. 2 and Fig. 3. A sectional view of the $SrTiO_3$ unit cell is depicted in Fig. 4.

2). The second reason of the obstacle in understanding of HTSC is due to a use of the stationary ion radii as it is accepted for classical ionic compounds (Fig. 1a) instead of the quantum superposition of the ground and ionized (excited) states (Fig. 1b). Electron properties of the oxide are determined by tunneling between these states¹). Their occupancy is inversely proportional to r^3 , where r is the given orbital radius. The metal atom ground state orbital occupancy is small $z_{Me} < 1$ (Fig. 1 b) that corresponds to the diluted metal limit ("chemical" dilution; a role of the ionicity and adiabatic effects is high). The electron density (taking into account the metal atom ground state occupancy $z_{Me} < 1$) can be not large enough for a transition of the system into the metal state and the electron pairs of the divalent atoms will survive, though their binding energy Δ_0 drops by a factor of ϵ^* down to the Δ_c value. The superconducting phase transition arises in this case due to the Bose-Einstein condensation (BEC) of the pairs not due to the Bardeen-Cooper-Schrieffer (BCS) mechanism. Notice that no pairs exist in univalent atoms. The BCS theory (ϵ_{Met}^*) does not explain superhigh transition temperatures and superlow (or vanishing) transition temperatures in univalent metals at standard conditions. The atomic electron pair binding energy (it equals $\Delta_0 = 5.2$ eV for Ba and $\Delta_0 = 10.1$ eV for Hg) decreases by a factor of $\epsilon^*(\Delta_c = \frac{\Delta_0}{\epsilon^*})$, when the atoms are moved together (here ϵ^* is the effective dielectric permeability of the medium containing Me^{2+} ions.) No such "relict" electron pairs exist in univalent metals. Properties of the medium change abruptly at metallization ($\epsilon^* \ll \epsilon_{Met}^*$) and atomic electron pairs give place (or transmute) to the Cooper ones. The "chemical" dilution

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¹ The quantum superposition of the ground and excited states (the atom remains neutral) takes place in atoms of the noble gases condensates and of the metals like Pd. Their metallization occurs due to tunneling over the excited states [4].

allows us to obtain stable systems at the state near to the metallization threshold [5]. The energy equality condition for electronic energies in the phases at the transition point $\frac{2.87(\frac{h}{2\pi})^2 n^{5/3}}{m^*} \sim \frac{\Delta_c n}{2}$ gives $T_{cmax} \sim \frac{\Delta_c}{5.5k}$ [5]. In $\text{YBa}_2\text{Cu}_3\text{O}_7$, $T_c = 90\text{ K}$; $r_{\text{Ba}} = 2.19\text{ \AA}$; $\varepsilon^* \sim 25$; $m^* \sim 5m_e$; $\Delta_c \sim 5.2/25 = 0.21\text{ eV} \sim 5.5kT_{cmax}$ [5]. That is why the real $T_c = 90\text{ K}$ is significantly less, than possible $T_{cmax} \sim 495\text{ K}$ and the transition has features of the Bose-Einstein condensation of hard electron pairs. An increase of the pair density n_2 will lead to a rise of T_c , but only up to 495 K , i.e. the system metallization temperature. Then ε^* changes abruptly, Δ_c drops, and the pairs transmute into the Cooper ones, while the transition acquires BCS character being accompanied by depairing [5].

3). A density of the "active" electrons can be estimated assuming that dilution is determined by occupancies of the metal atom orbitals, which depend on the acceptor properties of oxygen (or selen). The three-dimensional superconductivity occurs in result of tunneling over the electron quantum states of the metal atoms. An irregular network ("cobweb") of paths and rings [4, 6, 7] gives way probably to regular $3d$ lattice of superconducting threads ("gossamer") [8].

The metal and oxygen orbital occupancies are inversely proportional to the orbital volume $z_{\text{Me}}/z_{\text{O}} \sim (r_{\text{O}}/r_{\text{Me}})^3$ [5]. For the pair $\text{Se}^{2-} - \text{O}^{2-}$ we have $z_{\text{MeSe}} \sim 8z_{\text{MeO}}$. This gives for the BEC model the transition temperature increase of $8^{2/3} = 4$ times, i. e. up to 360 K that complies with the data [1]. Such electron pairs density corresponds to the composition $\text{YBa}_2\text{Cu}_3\text{O}_{7/8}$ (a metal alloy mixed with oxides). Replacement of Ba atoms with Hg ones ($\Delta_0 = 10.1\text{ eV}$; $r = 1.45\text{ \AA}$) leads to increase of the pair density by a factor of $(2.19/1.45)^3 \sim 3.4$ and of T_c up to $T_p \sim 200\text{ K}$. The BEC threshold increases up to $T_{cmax} \sim 1000\text{ K}$.

4). One oxygen atom falls at one metal atom in $\text{YBa}_2\text{Cu}_3\text{O}_7$. A number of electron pairs in the unit cell equals 2.5; each pair occupies the volume of 69.4 \AA^3 . If one takes into account the Ba atom orbital occupancy $z_{\text{Me}} \sim z_{\text{O}} (0.5/2.19)^3 = z_{\text{O}}/84$, the "active" electron pairs density takes the value of $n_2 \sim 1.7 \cdot 10^{20}\text{ cm}^{-3}$. In the BEC case $T_c = 92\text{ K}$ for $m^* \sim 5m_e$. The medium dielectric constant $\varepsilon^* \sim 20$.

5). In the case of SrTiO_3 , the atomic value $\Delta_{0\text{Sr}} = 5.7\text{ eV}$ becomes equal to $\Delta_c \sim 1.4 \cdot 10^{-4}\text{ eV}$ at $\varepsilon^* \sim 4 \cdot 10^4$ [9] and $T_{cmax} = \frac{\Delta_c}{5.5k} \sim 0.25\text{ K}$. An estimate of the intrinsic electron density basing on the orbital occupancy for the Sr atoms ($n \sim r^{-3}$) gives $n \sim 10^{20}\text{ cm}^{-3}$. This estimate is too rough since the Sr - O distance is distinctly larger, than $r_{\text{Sr}} + r_{\text{O}}$ (Fig. 4). Doping by Nb partly blocks the oxygen valence and increases the free electron pairs density given by Sr atoms ($\text{SrNb}_x\text{Ti}_{(1-x)}\text{O}_3$) [10]. T_c is proportional to $n^{2/3}$ up to $T_{cmax} = 0.28\text{ K}$ [10]. The temperature T_c falls abruptly after $T_{cmax} (n > 1 \cdot 10^{20}\text{ cm}^{-3})$; metallization occurs and BCS superconductivity establishes [11]. The function $T_c \sim n$ [10] is asymmetric and corresponds to the plot in Fig. 5. The electron effective mass equals about $1200 \cdot m_e$.

6). Atomic cores of the electron pairs participate in forming of the medium electronic properties (ε^*, m^*) of stoichiometric compounds. The metal atoms are diluted by oxygen ones. In nonstoichiometric (nanocomposite) HTSC compounds atoms and their electron pairs have contact only with atoms of the matrix (Fig. 3). The metal atoms are diluted by matrix. The electron pairs density and the binding energies in diatomic molecules are known for the "physical" dilution of metals in $\text{Ag}_2(\text{Ag}_3\text{Pb}_2\text{H}_2\text{O}_6)$ ($T_c \sim 400\text{ K}$; $m^* \sim 7.5m_e$) [3], in $(\text{Na}_2)_{0.02}\text{NH}_3$ ($T_c \sim 200\text{ K}$; $m^* \sim 5m_e$) [12] and in $(\text{Na}_2)_{0.025}\text{WO}_3$ ($T_c \sim 91\text{ K}$; $m^* \sim 10m_e$) [13]. This allows us to estimate the electron effective mass m^* basing on the BEC magnitude of T_c . There are $3d$ lattices of Ag_2 molecules chains or $3d$ networks of irregular Na_2 chains in these compounds. These chains seemingly weakly interact with the matrix. In result, the pair binding energy Δ_c is almost independent on the matrix ε^* . In the all of three cases, the pair binding energy can be estimated as $\Delta_c \sim 5.5kT_{cmax}$ [5]. The intermediate case between BEC and BCS occurs. The electron effective masses in the all of four systems [1, 3, 12, 13] are very near and can stem from the polaron (bipolaron) effect [14].

7). Parameters of some HTSC are given in the Table.

	$\text{YBa}_2\text{Cu}_3\text{O}_7$	$\text{YBa}_2\text{Cu}_3\text{Se}_7$	$\text{Ag}_2(\text{Ag}_3\text{Pb}_2\text{H}_2\text{O}_6)$	$(\text{Na}_2)_{0.025}\text{WO}_3$	$(\text{Na}_2)_{0.02}\text{NH}_3$
$T_c\text{ K}$	~ 90	371	~ 400	~ 90	~ 180
$T_{cmax}\text{ K}$	~ 500	~ 500	~ 500	~ 100	~ 200
$n_2\text{ cm}^{-3}$	$1.7 \cdot 10^{20}$	$13.6 \cdot 10^{20}$	$25.6 \cdot 10^{20}$	$4.74 \cdot 10^{20}$	$4.71 \cdot 10^{20}$
$\Delta_c\text{ eV}$	> 0.21	~ 0.173	~ 0.187	~ 0.043	~ 0.09
m^*/m_e	~ 5	~ 5	~ 7.5	~ 10	~ 5
ε^*	25(?) (90 K)	$\sim 25(?)$	$\sim (30 - 40)(?)$	$\sim 50(100\text{ K})$	25.4(200 K)

8). Conclusion.

"Physical" or "chemical" dilution of metals allows us to synthesize systems, intermediate between insulator and metal. A possibility to explain superconductivity of some systems as a result of the Bose-Einstein condensation of the

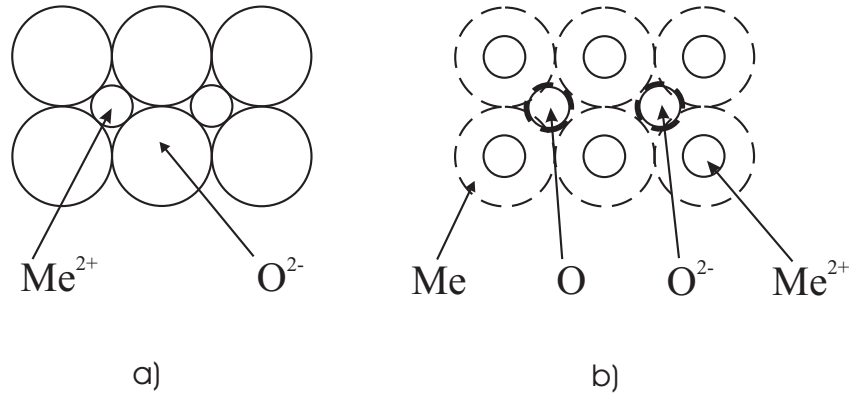


FIG. 1: Schematic representation of some possible structures of oxides:

- a) the O^{2-} ion radius is equal to $r_{O^{2-}} \sim 1.4 \text{ \AA}$;
b) $r_{O^{2-}} \sim r_O \sim 0.5 \text{ \AA}$ (Dilute metal).

electron pairs belonging to diatomic molecules formed by univalent atoms or the electron pairs of divalent atoms was shown above. However, an increase of T_c can be accompanied by instability or a quasi-one-dimensional structure can appear. Practically important superconductors must be 3-dimensional, have small ε^* , large Δ_c , have maximum density of homogeneously distributed electrons (before metallization). Synthesis of such materials must obey to a few physico-chemical conditions simultaneously. A directed physico-chemical "constructing" of superconductors can be most easily done in the case of nonstoichiometric systems - nanocomposites (a matrix filled with properly chosen atoms). Mg_xWO_3 ($\Delta_0 \sim 7.6 \text{ eV}$; $T_{cmax} \sim 600 \text{ K}$ at $x \sim (0.3 - 0.4)$) can be considered as one of examples of such materials, which is a nanocomposite unlike to MgB_2 . In the latter, Mg is diluted "chemically", the compound is a metal with the BCS type superconductivity. Several equilibrium Mg atom sublattices with $T_{cx} < 600 \text{ K}$ in the cavity lattice of WO_3 are possible.

The given here consideration show that synthesis of superconductors with $T_c > 300 \text{ K}$ is really possible.

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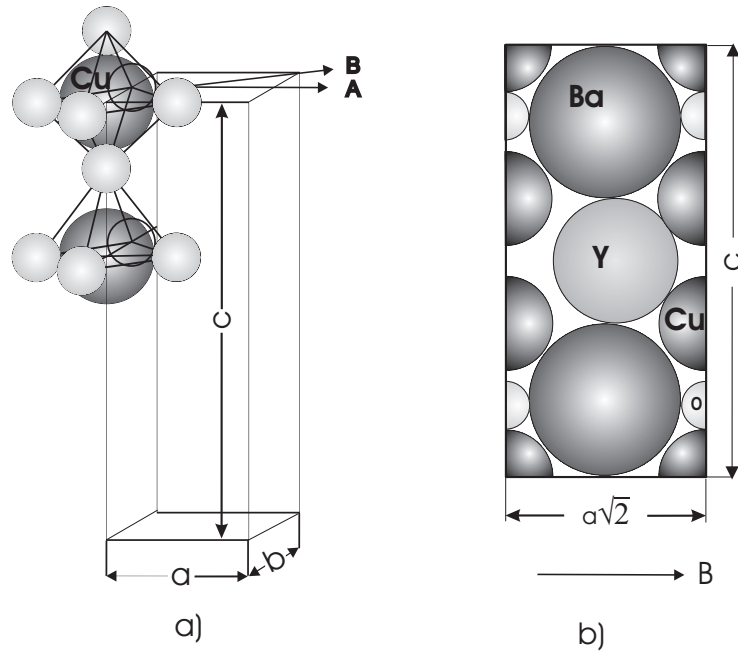


FIG. 2: a) the unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_7$, b) the cross section of the unit cell along B-direction.

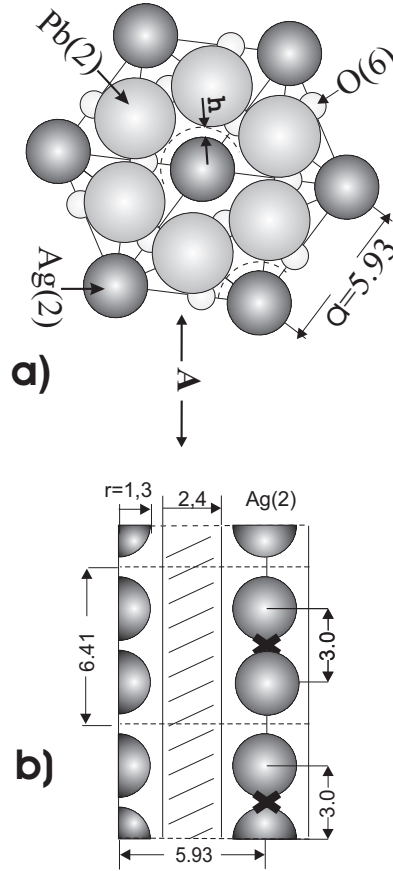


FIG. 3: Packing of atoms in $\text{Ag}_2(\text{Ag}_3\text{Pb}_2\text{H}_2\text{O}_6)$:
a) - a view along c -axis;
b) - 3D -lattice of quasionedimensional chains of Ag_2 molecules.

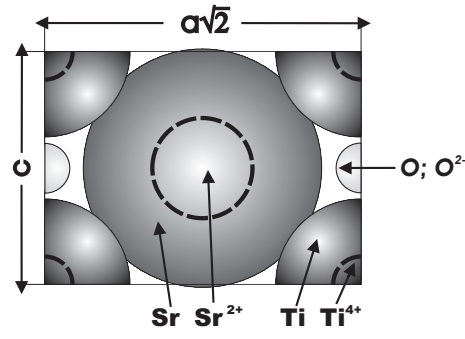


FIG. 4: A sectional view of the SrTiO_3 unit cell.

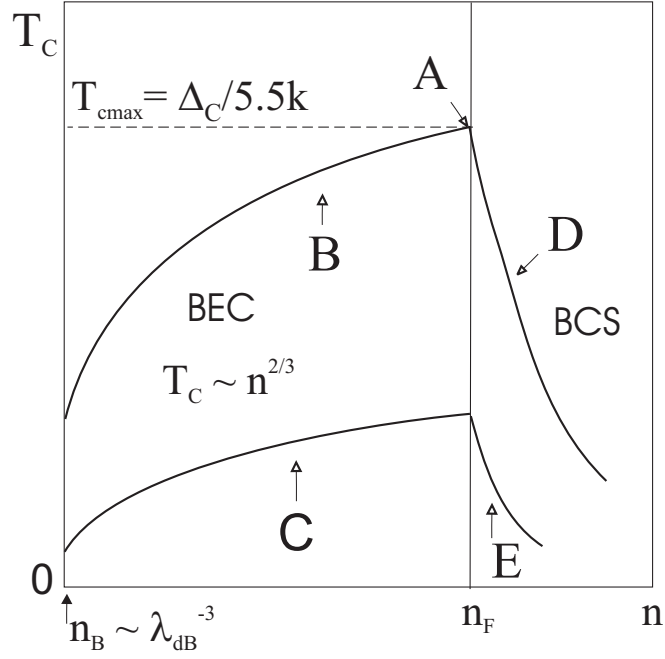


FIG. 5: Schematic representation of T_c dependance on the electron concentration for:

A — $\text{YBa}_2\text{Cu}_3\text{Se}_7$; $\text{Ag}_2(\text{Ag}_3\text{Pb}_2\text{H}_2\text{O}_6)$; $(\text{Na}_2)_{0.025}\text{WO}_3$; $(\text{Na}_2)_{0.02}\text{NH}_3$; $\text{SrNb}_y\text{Ti}_{(1-y)}\text{O}_3$; Mg_yWO_3 .

B — $\text{YBa}_2\text{Cu}_3\text{O}_7$; Mg_xWO_3 .

C — $\text{SrNb}_x\text{Ti}_{(1-x)}\text{O}_3$.

D — MgB_2 .

E — $\text{SrNb}_z\text{Ti}_{(1-z)}\text{O}_3$. ($x < y < z$)

λ_{dB} — the de Broglie wavelength.